Reactivity of a coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complex†

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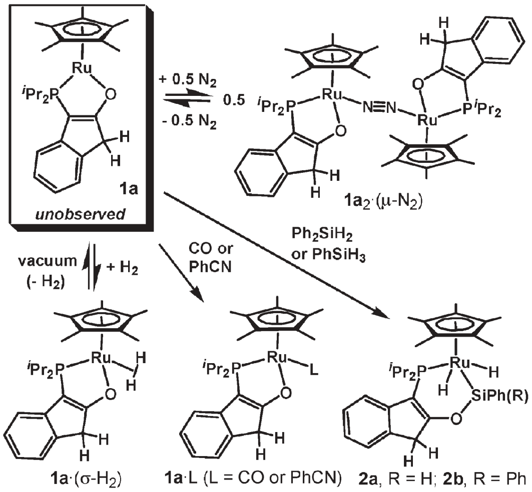
Whereas a new coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complex (1a) forms adducts with two-electron donors (including σ-H_2 and μ-N_2 ligands), double Si–H bond activation is observed upon treatment with Ph_2SiH_2 or $PhSiH_3$, leading to the clean formation of products corresponding to the net insertion of a Ph_2Si: or Ph(H)Si: fragment into the Ru–O bond of 1a.

Studies documenting the reactivity properties of coordinatively unsaturated (η^5-C_5R_5)RuL_n (η^5-C_5H_5 = Cp; η^5-C_5Me_5 = Cp*) species are of considerable significance, since complexes of this type represent key reactive intermediates in a range of prominent metal-catalyzed transformations.[1] Moreover, novel stoichiometric reactivity identified in the course of such investigations expands our understanding of the substrate transformations that can occur within the coordination sphere of unsaturated (η^5-C_5R_5)RuL_n species, thereby providing the basis for the development of new and/or mechanistically distinct metal-catalyzed reactivity.[2] While considerable insight has been gained through the investigation of both neutral Cp*RuL(X) complexes and $[Cp^*RuL_2]^+X^-$ salts,[1c,d] the examination of alternative classes of complexes supported by new ancillary ligands continues to advance our appreciation of how even subtle alterations to the ligand steric and/or electronic properties can influence the reactivity behavior of coordinatively unsaturated Cp*RuL_n species.

Reports documenting the reactivity of well-defined, coordinatively unsaturated Cp*RuL_n complexes supported by monoanionic, heterobidentate ligands are rare.[1,3] In this context, we have reported previously on our efforts to prepare the formally zwitterionic species, Cp*Ru(κ^2-3-*P*^{i}Pr_2-2-*N*Me_2-indenide); this complex alleviates coordinative unsaturation by rearranging to an 18-electron κ^2-*P*,*C* hydridocarbene complex *via* intramolecular, double geminal C–H bond activation involving a ligand NMe group.[4] In expanding upon this research, we sought to develop structurally related Ru complexes that might be capable of mediating intermolecular double geminal E–H bond activation processes (E = main group element). In consideration of the hard (N) and soft (P) donor ligands featured in the aforementioned zwitterion,[4] and given the beneficial reactivity properties imparted by anionic κ^2-*P*,*O* ligands on alternative classes of metal complexes,[5] we identified coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complexes supported by phosphinoenolate chelating ligands as appealing targets of inquiry. Although heterobidentate species of this type were unknown prior to this work, Caulton and co-workers have demonstrated that π-donation from oxygen in related Cp*RuPR_3(OR′) complexes can serve to stabilize such unsaturated species, and to promote metal-mediated substrate transformations.[6] Herein we provide a preliminary account of the reactivity of the new coordinatively unsaturated Cp*Ru(κ^2-*P*,*O*) complex **1a** (Scheme 1), with comparisons made to the structurally related monodentate species Cp*Ru(P^iPr_2Ph)(OCH_2CF_3) **1b**.[6] In addition to forming adducts with a number of two-electron donors (including σ-H_2 and μ-N_2 ligands), complex **1a** mediates double Si–H bond activation reactions involving Ph_2SiH_2 or $PhSiH_3$, affording products derived from the net insertion of Ph_2Si: or Ph(H)Si: fragments into the Ru–O bond of **1a**.

Treatment of 1-diisopropylphosphino-2-indanone with 0.25 $[Cp^*RuCl]_4$ afforded (κ^2-*P*,*O*-1-diisopropylphosphino-2-indanone)Cp*RuCl in 96% isolated yield, which in turn was spectroscopically and crystallographically characterized (Fig. 1);‡ the structural features noted in this complex compare well with those found in a related (κ^2-*P*,*O*)Cp*RuCl compound.[7] In the pursuit of **1a**, a deep red solution of (κ^2-*P*,*O*-1-diisopropylphosphino-2-indanone)Cp*RuCl in benzene was treated with NaN$(SiMe_3)_2$; ^{31}P NMR analysis of the resulting dark green solution revealed the quantitative conversion to a single phosphorus-containing product (**1a**$_2$·(μ-N_2); δ ^{31}P = 50.1 ppm, $\Delta\nu_{1/2}$ = 213 Hz, C_6D_6, 300 K), which was isolated in 78% yield (Scheme 1).[8a] The assignment of this product as the new dinuclear



Scheme 1 Reactivity of **1a** with small molecule substrates.

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† Electronic supplementary information (ESI) available: Experimental details and characterization data, including crystallographic data for (κ^2-*P*,*O*-1-diisopropylphosphino-2-indanone)Cp*RuCl·0.5C_6H_6, **1a**$_2$·(μ-N_2) and **2b**. See DOI: 10.1039/b713386c

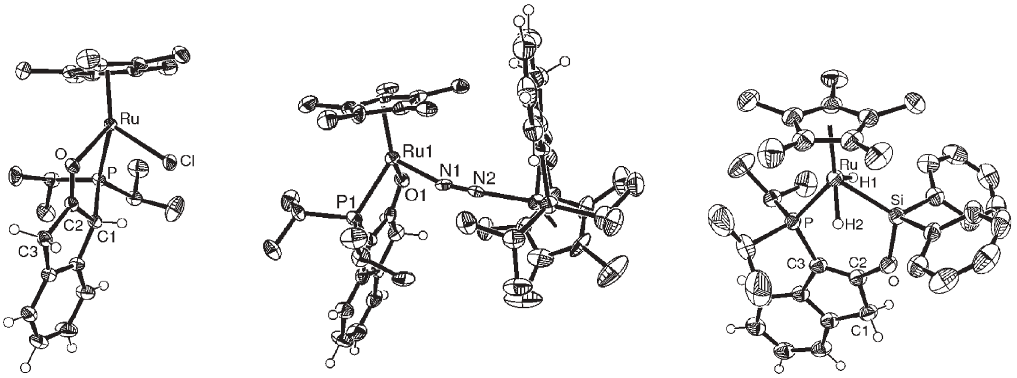

Fig. 1 ORTEP diagrams for (κ^2-*P*,*O*-1-$P^i Pr_2$-2-indanone)Cp*RuCl·$0.5C_6H_6$ (left), $\mathbf{1a}_2$·(μ-N_2) (middle), and **2b** (right), shown with 50% ellipsoids. The benzene solvate and selected H-atoms have been omitted for clarity. Bond lengths (Å) for (κ^2-*P*,*O*)Cp*RuCl: Ru–P 2.3421(6); Ru–O 2.220(2); Ru–Cl 2.4508(6); $^iPr_2P$–C 1.873(2); C–O 1.228(3); C1–C2 1.505(3); C2–C3 1.508(3). Bond lengths (Å) and angles (°) for $\mathbf{1a}_2$·(μ-N_2): Ru–N 1.996(7), 1.994(7); Ru–O 2.147(6), 2.151(6); Ru–P 2.360(2), 2.370(3); C–O 1.31(1), 1.29(1); C2–C3 1.39(1), 1.38(1); $^iPr_2P$–C 1.763(8), 1.797(9); N–N 1.131(8); Ru–N–N 165.5(7), 163.5(6). Bond lengths (Å) for **2b**: Ru–P 2.3081(5); Ru–Si 2.3102(6); Si–O 1.705(2); C–O 1.333(3); C2–C3 1.360(3); $^iPr_2P$–C 1.820(2).

phosphinoenolate complex $\mathbf{1a}_2$·(μ-N_2) was ultimately achieved by use of single-crystal X-ray diffraction techniques (Fig. 1).‡ Notably, $\mathbf{1a}_2$·(μ-N_2) represents a rare example of a (η^5-C_5R_5)RuL_n complex featuring a bridging dinitrogen ligand.[1c,9] The Ru–N and N–N distances as well as the modestly non-linear Ru–N–N fragments found in $\mathbf{1a}_2$·(μ-N_2) compare well with those of $[(CpRuP_2)_2\cdot(\mu\text{-}N_2)]^{2+}$ dications reported by Valerga and co-workers.[10] While no N–N stretch is observed in the IR spectrum of $\mathbf{1a}_2$·(μ-N_2), the Raman spectrum of this complex features a band at 2042 cm^{-1} attributable to the μ-N_2 unit.[10] By comparison, the isolable monodentate complex **1b** apparently does not exhibit a propensity to coordinate dinitrogen.[6a] In contrast to the rather short Ru–O distance observed in the coordinatively unsaturated species Cp*Ru(PCy_3)(OCH_2CF_3) (1.992(10) Å),[6a] the elongated Ru–O distances in $\mathbf{1a}_2$·(μ-N_2) suggest that π-donation from oxygen is negligible in this dinuclear complex, in keeping with the adduct Cp*Ru(PCy_3)(OCH_2CF_3)(CO) (Ru–O 2.090(3) Å).[6a] The ability of $\mathbf{1a}_2$·(μ-N_2) to serve as a reactive source of **1a** was demonstrated upon exposure to an atmosphere of CO, or two equiv. of PhCN; in both cases, the corresponding **1a**·L adduct (L = CO, 93%; L = PhCN, 91%) was obtained. The observation of nearly identical C–O stretching frequencies in the IR spectra of **1a**·CO (1903 cm^{-1}) and Cp*Ru(P^iPr_2Ph)(OCH_2CF_3)(CO) (1906 cm^{-1})[6d] indicates that the P,O ligand sets in these related complexes have comparable electron-donating abilities.

Interest in the reactivity of coordinatively unsaturated (η^5-C_5R_5)RuL_n complexes with H_2 and silanes can be attributed to the potential involvement of such reaction steps in homogeneous catalytic reaction cycles.[1,2,11] Notably, the course of such reactions has been found to be dependent on the nature of the ancillary ligand(s). For example, whereas Cp*RuP^iPr_3(Cl)[12] and $[Cp^*Ru(\kappa^2\text{-}NMe_2CH_2CH_2NMe_2)]^+X^-$[13] are unreactive toward H_2, related $[Cp^*RuP_2]^+X^-$ complexes react to give $[Cp^*RuP_2(H)_2]^+X^-$; in some cases, non-classical $[Cp^*RuP_2(\sigma\text{-}H_2)]^+X^-$ species exist in equilibrium with the dihydride product, or are detected spectroscopically at low temperatures as reactive intermediates.[1c,11] Given the differing reactivity exhibited by these related complexes featuring either N- or P-based ligands, we became interested in examining the behavior of the 'hard–soft' chelate complex **1a** with H_2 and silane substrates. Exposure of a degassed toluene-d_8 solution of $\mathbf{1a}_2$·(μ-N_2) to an atmosphere of H_2 at 24 °C resulted in the quantitative formation of a single phosphorus-containing product (**1a**·(σ-H_2); δ ^{31}P = 65.2 ppm, $\Delta\nu_{1/2}$ = 180 Hz, toluene-d_8, 300 K).[8a] Our assignment of this product as a non-classical dihydrogen adduct, rather than a dihydride complex, was made initially based on the observation of a broad ^1H NMR resonance centered at −5.7 ppm; variable-temperature NMR data obtained for this complex, including the rather short $T_{1(\min)}$ relaxation value (17 ms, 218 K, 250 MHz) associated with the dihydrogen ligand, confirmed this structural assignment.[11] Conversely, Caulton and co-workers[6c] have noted that treatment of **1b** with <2 equiv. H_2 under similar conditions afforded Cp*Ru(P^iPr_2Ph)(OCH_2CF_3)$(H)_2$, while the addition of excess H_2 produced $HOCH_2CF_3$ and the trihydride Cp*Ru(P^iPr_2Ph)$(H)_3$. Despite this divergent reactivity, it is interesting to note that both **1a**·(σ-H_2) and Cp*Ru(P^iPr_2Ph)(OCH_2CF_3)$(H)_2$ liberate H_2 upon exposure to vacuum. The facile loss of H_2 from **1a**·(σ-H_2) has thus far prevented the isolation of this complex.

In monitoring the progress of the reaction of $\mathbf{1a}_2$·(μ-N_2) with 2 equiv. $PhSiH_3$ in C_6D_6 by use of NMR methods, the consumption of the starting materials was noted after 15 min, along with the formation of three phosphorus-containing products, one of which being **2a**. Subsequent analysis of the reaction mixture (^{31}P NMR) after a total of 3 h revealed the quantitative formation of **2a**, which in turn was isolated in 95% yield. Under similar conditions employing 2 equiv. Ph_2SiH_2, **2b** was formed quantitatively after only 15 mins, thereby allowing for the isolation of this complex in 95% yield.[8b] The assignment of **2a** and **2b** as products derived from double geminal Si–H bond activation and net insertion of a Ph(H)Si: or Ph_2Si: fragment into the Ru–O bond of **1a** is in keeping with the ^1H, ^{13}C and ^{29}Si NMR spectra obtained, including the observation of two Ru–*H* signals (−11.14 and −11.92 ppm) and an Si–*H* resonance in the ^1H NMR spectrum of the C_1-symmetric **2a**, as well as a single ^1H NMR resonance (−11.02 ppm) attributable to the equivalent Ru–*H* ligands in the C_S-symmetric **2b**. The crystallographically determined structure of **2b** (Fig. 1)‡ exhibits Ru–Si and Si–O distances that are in keeping with those found in related complexes featuring bidentate Ru(κ^2-*Si*$Ph_2OC_5H_4$*N*) and Ru(κ^2-*Si*Ph_2OC(Me)=*O*) ligands.[14] Notably, the long Ru–*H*···*Si* contacts observed in the structure of **2b** (*ca.* 2.12 Å and 2.14 Å), along with the relatively low measured $^2J_{\mathrm{SiH}}$ values (**2a**: 9.4 Hz; **2b**: 9.8 Hz),[15] support the view of **2a** and **2b** as being classical dihydride complexes. In the absence of conclusive experimental data we are unable to comment definitively on the mechanism of this transformation. However, we favor a process involving initial intermolecular Si–H oxidative addition to **1a**, Si–O reductive elimination, and finally intramolecular Si–H oxidative addition involving the tethered silyl ether fragment.[8c] The absence of observable chemical exchange (^{1}H EXSY) involving the Ru–*H* and Si–*H* groups of **2a** suggests that if the intramolecular Si–H oxidative addition to Ru in such a mechanistic scenario is reversible, this Si–H addition–elimination process occurs at a rate that is slow relative to the dynamic exchange NMR timescale. In keeping with our proposed mechanism for the formation of **2a,b**, Caulton and co-workers[6c] observed that treatment of **1b** with Ph_2SiH_2 generated a 1 : 1 mixture of $Cp^*Ru(P^iPr_2Ph)(H)_2(SiXPh_2)$ (X = H or OCH_2CF_3) as the Ru-containing products. In rationalizing the formation of these two products, $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)(H)(SiHPh_2)$ was invoked as the first-formed oxidative addition product; upon elimination of $Ph_2Si(H)(OCH_2CF_3)$, the resultant coordinatively unsaturated reactive intermediate $Cp^*Ru(P^iPr_2Ph)(H)$ could undergo an intermolecular Si–H oxidative addition with either $Ph_2Si(H)(OCH_2CF_3)$ or additional Ph_2SiH_2 to afford the two observed Ru products. By comparison, tethering of the silyl ether fragment to the phosphine donor that occurs during the reaction of **1a** with Ph_2SiH_2 in our proposed mechanism sets up an intramolecular Si–H addition, leading to the clean formation of **2b**. The observed stoichiometric reaction steps may be of relevance to the Ru-mediated alcoholysis of silanes.[16]

In summary, a preliminary account of the reactivity of the new coordinatively unsaturated $Cp^*Ru(\kappa^2\text{-}P,O)$ complex **1a** has been provided. Notably, the reactivity profile of **1a** has been found to differ from that of the monodentate complex $Cp^*Ru(P^iPr_2Ph)(OCH_2CF_3)$ (**1b**),[6] as well as some other established classes of coordinatively unsaturated Cp^*RuL_n species. Encouraged by these observations, and given the paucity of coordinatively unsaturated Cp^*RuL_n complexes supported by monoanionic, heterobidentate ligands, we are exploring further the stoichiometric reactivity of **1a** and related derivatives and will report on these studies in due course.

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Notes and references

‡ Selected crystallographic data for (κ^2-*P*,*O*-1-diisopropylphosphino-2-indanone)$Cp^*RuCl\cdot 0.5C_6H_6$ ($C_{28}H_{39}Cl_1O_1P_1Ru_1$, 559.08 $\mathrm{g\,mol^{-1}}$): a = 20.2188(2) Å, b = 8.5282(3) Å, c = 16.0143(3) Å, β = 105.8122(10)°, V = 2656.86(11) Å^3, T = 173($\pm$2) K, space group = $P2_1/c$ (monoclinic), Z = 4, independent reflections = 6346 (R_{int} = 0.0417), GOF = 1.076, R_1 = 0.0324 ($F_o^2 > 2\sigma(F_o^2)$), wR_2 = 0.0783 (all data). Selected data for $\mathbf{1}_2\cdot(\mu\text{-}N_2)$ ($C_{50}H_{70}N_2O_2P_2Ru_2$, 995.16 $\mathrm{g\,mol^{-1}}$): a = 17.4049(11) Å, b = 13.5276(8) Å, c = 23.1490(19) Å, β = 118.873(3)°, V = 4772.8(6) Å^3, T = 173($\pm$2) K, space group = $P2_1/c$ (monoclinic), Z = 4, independent reflections = 5742 (R_{int} = 0.1289), GOF = 1.023, R_1 = 0.0557 ($F_o^2 > 2\sigma(F_o^2)$), wR_2 = 0.1136 (all data). Selected data for **2b** ($C_{37}H_{47}O_1P_1Ru_1Si_1$, 667.88 $\mathrm{g\,mol^{-1}}$): a = 13.0305(12) Å, b = 14.5399(13) Å, c = 17.6901(16) Å, V = 3351.6(5) Å^3, T = 193($\pm$2) K, space group = $P2_12_12_1$ (orthorhombic), Z = 4, independent reflections = 7686 (R_{int} = 0.0224), GOF = 1.098, R_1 = 0.0270 ($F_o^2 > 2\sigma(F_o^2)$), wR_2 = 0.0712 (all data). CCDC 654073 for (κ^2-*P*,*O*-1-diisopropylphosphino-2-indanone)$Cp^*RuCl\cdot 0.5C_6H_6$, 654074 for $\mathbf{1}_2\cdot(\mu\text{-}N_2)$ and 654072 for **2b**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b713386c

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